

# ADVANCED INORGANIC CHEMISTRY

*A Comprehensive Text*

---

F. ALBERT COTTON

ROBERT A. WELCH DISTINGUISHED PROFESSOR OF CHEMISTRY  
TEXAS A AND M UNIVERSITY  
COLLEGE STATION, TEXAS, USA

and

GEOFFREY WILKINSON

SIR EDWARD FRANKLAND PROFESSOR OF INORGANIC CHEMISTRY  
IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY  
UNIVERSITY OF LONDON, ENGLAND

*Fourth Edition, completely revised from the original literature*

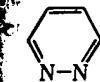
A WILEY-INTERSCIENCE PUBLICATION

JOHN WILEY & SONS  
New York • Chichester • Brisbane • Toronto • Singapore

APPENDIX C

Other Nitrogen Heterocycles<sup>28</sup>

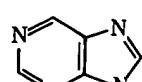
In addition to bipyridine and related heterocycles, there are numerous other heterocycles that give uni- or multidentate complexes. Some of the more important are:



Pyridazine



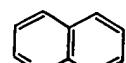
Pyrimidine



Purine



Pyrazine



1,8-Naphthyridine



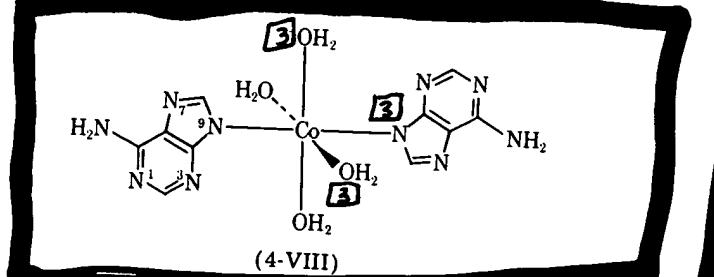
Pyrazolate



Imidazolate

One of the most important areas of concern for metal binding with nucleotides, purines, and pyrimidines arises because of their presence in nucleic acids.<sup>29</sup> The coordination of certain metal complexes, notably *cis*-PtCl<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>, as anticancer agents, is believed to arise through binding to nucleic acids. Other aspects of the binding of metals to nucleic acid include the attachment of lanthanide ions as shift reagents for fluorescent probes and the use of heavy metals to assist in X-ray structural determinations.

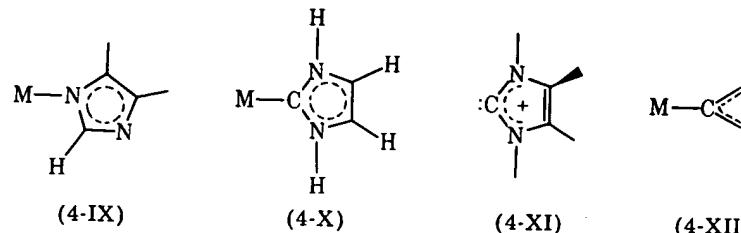
unsubstituted purine, the major liability for coordination is the imidazole ring (N-9), which is protonated in the free neutral ligand. An example is the complex of adenine, [Co(ad)<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>]<sup>+</sup> (4-VIII).



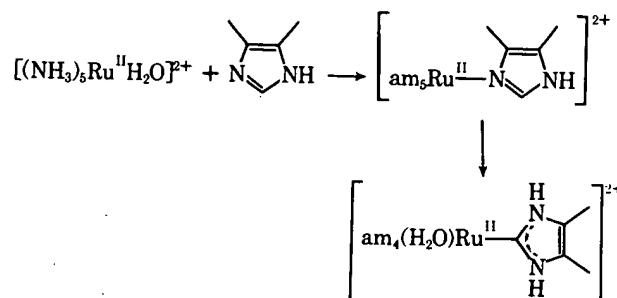
See and M. Kubo, *Coord. Chem. Rev.*, 1976, **21**, 1; B. C. Bunker et al., *J. Am. Chem. Soc.*, 1976, **98**, 3665; V. E. Hatfield, J. C. S. Dalton, 1978, 368 (pyridazine, pyrazine); J. G. Vos and J. Groenveld, *Inorg. Chim. Acta*, 1978, **27**, 173 (pyrazolate).  
 Fischer and R. Bau, *Inorg. Chem.*, 1978, **17**, 27; D. J. Hodgson, *Prog. Inorg. Chem.*, 1977, **11** (stereochemistry of complexes); L. G. Marzilli, *Prog. Inorg. Chem.*, 1977, **23**, 256 (metal interactions); L. G. Marzilli and T. J. Kistenmacher, *Acc. Chem. Res.*, 1977, **10**, 146; G. Matikakis et al., *Inorg. Chem.*, 1978, **17**, 915 (Pd<sup>II</sup>).

If the 9-position is blocked, the other imidazole nitrogen, N-7, is core. Binding appears somewhat less likely through N-1 than through N-7; three complexes established by X-ray crystallography, two also involve with both N-1 and N-7.

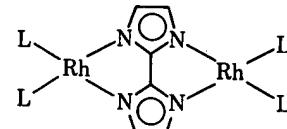
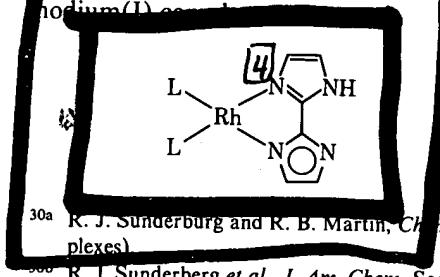
Imidazoles<sup>30a</sup> have been widely studied. Although the binding is usually the N atom (4-IX), in some Ru<sup>II</sup>, Ru<sup>III</sup>, Fe<sup>0</sup>, and Cr<sup>0</sup> complexes it is p. have C-bonded groups<sup>30b</sup> (4-X).



The C-bonded entity can be regarded as a carbene (4-XI) (see Chapter a C-bound amidine<sup>31</sup> (4-XII). An example of a C-bonded species is the um(II) complex obtained as follows:



The N-bonded imidazoles commonly form bridges between two metal as in  $[\text{Cu}_3(\text{imH})_2(\text{im})_2]^{14+}$  and in  $\{(\text{Pn}(\text{im})(\text{TPP})\text{THF}\}_n$ , where TPP phenylporphyrin. Biimidazoles can act as mono or dianions,<sup>33</sup> for example, sodium(I) complexes.



<sup>30a</sup> R. J. Sunderburg and R. B. Martin, *Chem. Rev.*, 1974, **74**, 471 (imidazole and histic complexes).

<sup>500</sup> R. J. Sunderberg *et al.*, *J. Am. Chem. Soc.*, 1974, **96**, 381; *Inorg. Chem.*, 1977, **16**, 1. Isied and H. Taube, *Inorg. Chem.*, 1976, **15**, 3070.

<sup>31</sup> D. J. Doonan, J. E. Parks, and A. J. Balch, *J. Am. Chem. Soc.*, 1976, **98**, 2120.

<sup>32</sup> G. Kolks *et al.*, *J. Am. Chem. Soc.*, 1976, **98**, 5720; J. T. Landrum *et al.*, *J. Am. Chem. Soc.*,

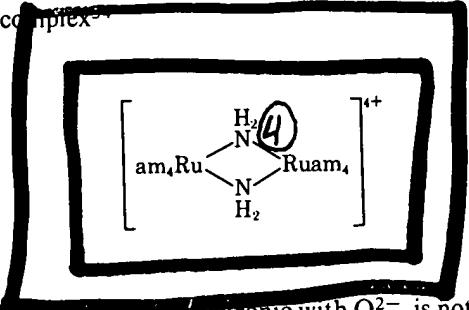
<sup>33</sup> S. W. Kaiser *et al.*, *Inorg. Chem.*, 1979, **18**, 2681.

## 4-12. Ligands Derived by Deprotonation of Ammonia and Amines:

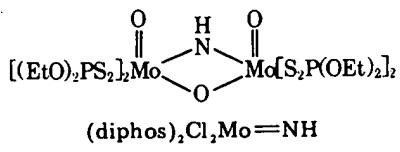
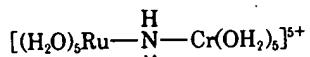
## Dialkylamido, Nitrene, and Nitrido Complexes

Ammonia can be deprotonated by alkali metals to give the anions  $\text{NH}_2^-$ ,  $\text{NH}^{2-}$ , and  $\text{N}^{3-}$ , and all of these species can act as ligands.

There are numerous examples of the *amido* ligand  $\text{NH}_2$  acting as a bridge, as in the ruthenium complex<sup>34</sup>



The *imido* ion  $\text{NH}^-$ , which is isoelectronic with  $\text{O}^{2-}$ , is not common as a ligand, though its alkyl and aryl derivatives  $\text{NR}$  are (see below). Some examples<sup>35</sup> of complexes, which have terminal or bent bridged NH groups, are the following species:



*Nitrido Complexes* have  $\text{N}^{3-}$  bound in the following ways:

*Multiply Bonded Nitride  $\text{M}\equiv\text{N}$* <sup>36</sup> Here the nitride ion is forming three equivalent bonds to the metal; it is one of the strongest  $\pi$  donors known. The compounds are rather similar to those containing  $\text{M}=\text{O}$  groups (Section 4-23). The complexes are largely those of molybdenum, tungsten, rhenium, ruthenium, and osmium, examples being  $\text{NReCl}_2(\text{PPh}_3)_2$ ,  $[\text{NOsCl}_5]^{2-}$ , and  $[\text{NOsO}_3]^-$ . The  $\text{M}\equiv\text{N}$  bonds are very short (ca. 1.16 Å) and the  $\text{M}-\text{N}$  stretching frequencies are in the region 950–1180  $\text{cm}^{-1}$ .

*N-Bridged Species.* These are of the following types:

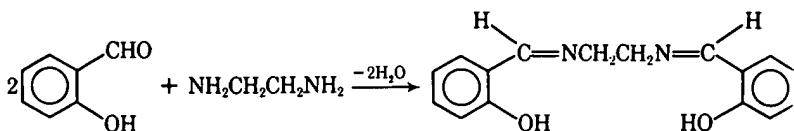
M. T. Flood *et al.*, *Inorg. Chem.*, 1973, **12**, 2153.

R. P. Cheney and J. N. Armor, *Inorg. Chem.*, 1977, **16**, 3338; A. W. Edelblut, B. L. Haymore,

and R. A. D. Wentworth, *J. Am. Chem. Soc.*, 1978, **100**, 2250.

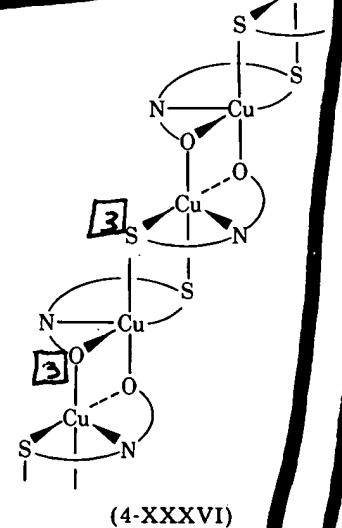
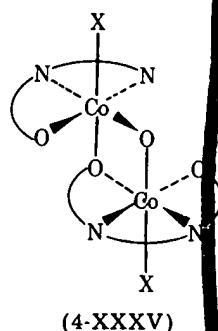
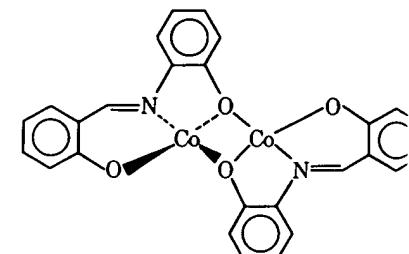
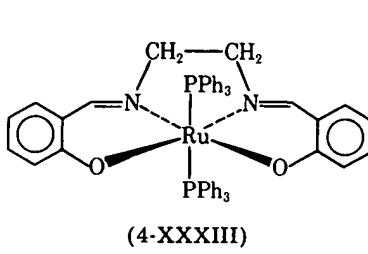
W. P. Griffith, *Coord. Chem. Rev.*, 1972, **8**, 369. D. Pawson and W. P. Griffith, *J.C.S. Dalton*, 1973, 417; C. D. Cowman *et al.*, *Inorg. Chem.*, 1976, **15**, 1747.

One of the best known Schiff base ligands is bis(salicyclaldehyde)ethylenimine<sup>88</sup> (sal<sub>2</sub>en):



This is a bifunctional (two OH groups), tetradentate ( $2N, 2O$ ) ligand. Other bases can be mono-, di-, or tetrafunctional and can have dentencies of 6 or with various donor atom combinations (e.g., for quinquedentate,  $N_3O_2$ ;  $N_2O_2P$ ;  $N_2O_2S$ , etc.). Complexes of un-ionized or partly ionized Schiff bases are also known<sup>89</sup> (e.g.,  $LaCl_3sal_2enH_2\cdot aq$ ).

Some representative types of complex that illustrate not only the formation of mononuclear but of binuclear and polymeric species are 4-XXXIII to 4-XXXVI.



<sup>88</sup> M. D. Hobday and T. D. Smith, *Coord. Chem. Rev.*, 1972-1973, 9, 311.

<sup>89</sup> J. I. Bullock and H.-A. Tajmir-Riahi, *J. C. S. Dalton*, 1970, 2035.

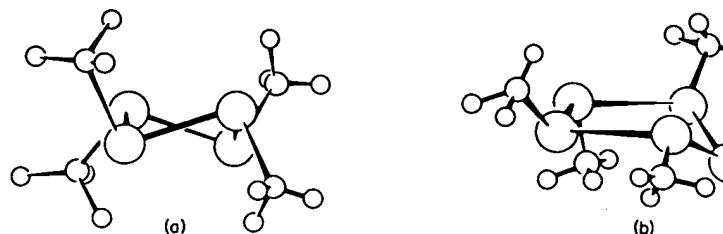
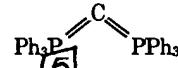


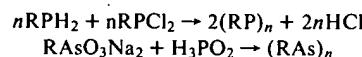
Fig. 14-11. The structures of (a)  $(CF_3P)_4$  and (b)  $(CF_3P)_5$ . Large, medium, and small circles represent P, C, and F atoms, respectively.

proper must be linear ( $P-C=C=CR_2$ ), there is  $d$ -orbital participation in phosphorus compounds, which are bent<sup>67</sup>.

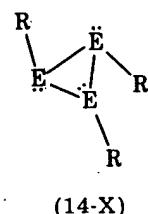


**Cyclopolyphosphines and -arsines.**<sup>68</sup> These are compounds of general formulas  $(RP)_n$  and  $(RAs)_n$ ,  $n = 3$  to 6.  $(C_2F_5P)_3$  is best known for  $n = 3$  and  $(PhAs)_6$ , and the three isomers  $[(MeC_6H_4)_2As]_6$  for  $n = 6$ . The four-membered rings predominate, with four-membered ones being favored substituents. The puckered structures adopted by these rings are representative compounds in Fig. 14-11.

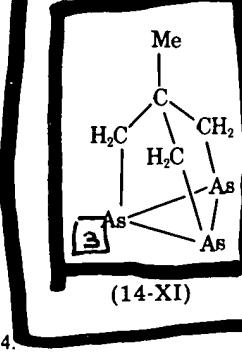
These compounds in general are thermally stable, though often reactive. Preparative reactions are:



The preferred conformation<sup>69</sup> for  $R_3E_3$  is 14-X, but as might be expected, an arrangement is enforced in 14-XI.<sup>70</sup>



(14-X)



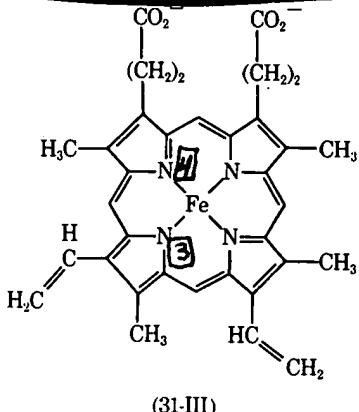
(14-XI)

<sup>67</sup> P. J. Carroll and D. D. Titus, *J.C.S. Dalton*, 1977, 824.

<sup>68</sup> L. R. Smith and J. R. Mills, *J. Organomet. Chem.*, 1975, 84, 1; *J. Am. Chem. Soc.*, 1975, 97, 3852.

<sup>69</sup> M. Baudler *et al.*, *Z. Naturforsch.*, 1976, 31b, 1305, 1311.

<sup>70</sup> J. Ellermann and H. Schossner, *Angew. Chem., Int. Ed.*, 1974, 13, 601.



00, consists of four myoglobinlike subunits; these four are similar but not all identical, two being  $\alpha$  units and the other  $\beta$  units. Neither the  $\alpha$  nor the  $\beta$  units of myoglobin have amino acid sequences that match the sequence in myoglobin, but nevertheless the ways in which the chains are coiled to give three-dimensional structures (tertiary structure) are quite similar. In each subunit of hemoglobin and myoglobin, the iron atom is also bonded to the nitrogen atom from the imidazole chain of a histidine residue. Figure 31-4 gives a schematic representation of  $\beta$ -subunit of hemoglobin; its essential features are typical of  $\alpha$ -subunits and  $\beta$ -globin as well.

According to the description above, the iron atoms in Hb and Mb when no oxygen is present (the deoxy forms) would be five-coordinate. In fact, there is probably another molecule loosely bonded in the sixth position (i.e., trans to the histidine nitrogen atom) to complete a distorted octahedron. The iron atom appears to be  $\beta$  the porphyrin plane toward the histidine. In both deoxy-Mb and deoxy-Hb the iron atoms are high-spin  $\text{Fe}^{II}$ , with four unpaired electrons.

The function of both Hb and Mb is to bind oxygen, but their physiological roles are very different. Hb picks up oxygen in the lungs and carries it to tissues via the circulatory system. Cellular oxygen is bound by myoglobin molecules that store it until it is required for metabolic action, whereupon they release it to other actors. Hb has an additional function, however, and that is to carry  $\text{CO}_2$  back to the lungs; this is done by certain amino acid side chains, and the heme groups are not directly involved. Because the circumstances under which Hb and Mb are ready to bind and release  $\text{O}_2$  are very different, the two substances have quite different binding constants as a function of  $\text{O}_2$  partial pressure (Fig. 31-5).

Myoglobin is not simply a passive carrier of oxygen but an intricate molecular machine. This may be appreciated by comparing its affinity for  $\text{O}_2$  to that of hemoglobin. For myoglobin (Mb) we have the following simple equilibrium:

$$\text{Mb} + \text{O}_2 \rightleftharpoons \text{MbO}_2 \quad K = \frac{[\text{MbO}_2]}{[\text{Mb}][\text{O}_2]}$$

$K$  represents the fraction of myoglobin molecules bearing oxygen and  $P$  represents

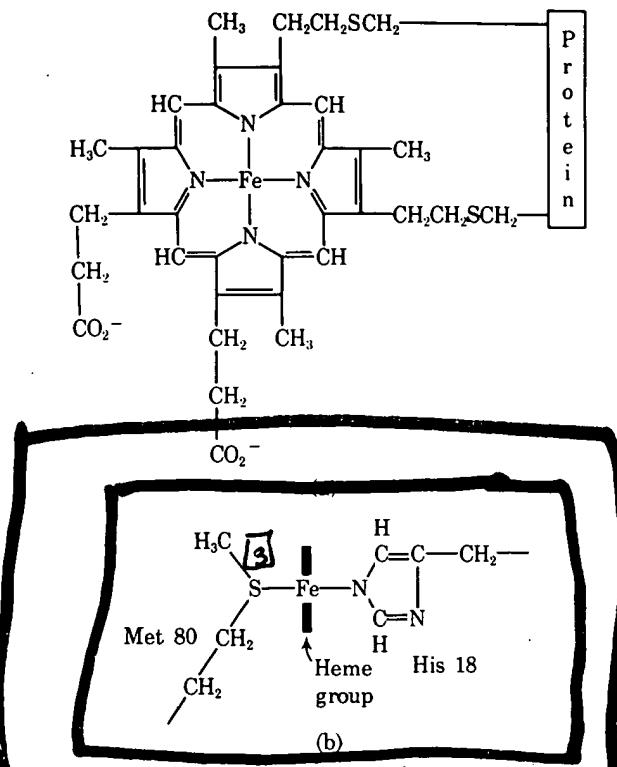
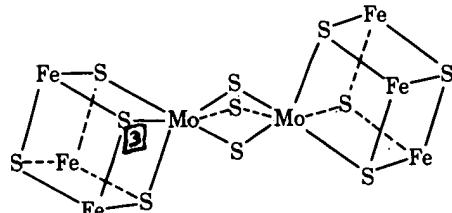


Fig. 31-8. (a) Mode of attachment of porphyrin ring to protein; (b) Coordination of the iron atom in cytochrome *c*.

tunnelling through the protein, by an outer-sphere mechanism. The folding of the protein chain is such that aside from the methionine and histidine residues that coordinate to the iron atom, the side chains that lie inside facing the heme group are the hydrophobic ones. The polar or charged side chains lie on the outside and are arranged in a unique pattern that seems to be designed to allow appropriate matching with both Cyt *c*<sub>1</sub> from which an electron must be accepted and cytochrome oxidase to which an electron must be transferred.

Cytochrome *c* seems to be one of the most ancient of biomolecules, having evolved in essentially its present form more than 1.5 billion years ago, even though it is present in all animals and plants, including those that have appeared more recently. It has been found that the cytochrome *c* of any eucaryotic species (one having cells with nuclei) will react with the cytochrome oxidase of any other species, thus confirming that this electron transfer chain has resisted evolutionary change for a very long time.

**Cytochrome P<sub>450</sub> Enzymes.** These heme proteins, found in cell membranes, catalyze the hydroxylation of C—H bonds; the name given to them is thus misleading, since they do not serve the type of electron transfer function just discussed for the "regular" cytochromes, but are actually enzymes. They consist of one heme



31-17. A schematic drawing of the type of Mo-Fe-S clusters in models for the Fe-Mo-Co of nitrogenase.

established their structures by X-ray crystallography.<sup>45,46</sup> The essential features of these structures are shown in Fig. 31-17. There is an  $RS^-$  ligand attached to each of the six iron atoms, as in the  $Fe_4S_4(SR)_4$  systems. Perhaps the most remarkable and important observation<sup>45</sup> concerning these model systems is that one of them has an Mo EXAFS pattern that is essentially superimposable on that for the Mo-co.

#### -11. Miscellaneous Other Metals

**The Alkaline Earths.** Only magnesium and calcium have biological roles; the other alkaline earths are more or less toxic.

**Magnesium** has several important biochemical functions. Its presence in chlorophyll, and the structure and photosynthetic activity of chlorophyll, have been mentioned (p. 284). Animal organisms also require magnesium. For example, an adult human body normally contains about 20 g, of which about half is found in the bones and the other half within cells. The major role of intracellular magnesium is to act as a cofactor for various enzymes that catalyze the hydrolysis or cleavage of polyphosphates. Among these are alkaline phosphatase (which is a zinc metalloenzyme as mentioned earlier), ATPase, hexokinase, and one or more of the nucleases. The  $Mg^{2+}$  ion functions as a Lewis acid, polarizing the phosphate groups, thereby enhancing the possibility of nucleophilic attack on a terminal phosphorus atom.

**Calcium** is found almost entirely (*ca.* 98%) in the bones, but it has several other roles as well. It is intimately involved in the process of muscle contraction, in neuron excitability, and in at least one part of the visual process. Calcium is also believed to be an integral part of biological membranes. Several enzymes (e.g.,  $\alpha$ -amylase and thermolysin) use  $Ca^{2+}$  ions in support of their structures, and in at least one case, trypsin, the  $Ca^{2+}$  ion has been shown to participate directly in the active site, where it is coordinated by an octahedral set of oxygen atoms.<sup>47</sup>

There are several proteins whose function appears to be calcium storage and transport, especially in conjunction with its role in muscle contraction. The best

R. H. Holm *et al.*, *J. Am. Chem. Soc.*, 1978, **100**, 4630.

C. D. Garner *et al.*, *J.C.S. Chem. Comm.*, 1978, 740.

F. A. Cotton and E. E. Hazen, Jr., *Proc. Nat. Acad. Sci. (U.S.)*, 1979, **76**, 2551.